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B.M. Penetrante, M.C. Hsiao, B.T. Merritt, G.E. Vogtlin

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Recent Studies suggest that the conversion of NO to NO2 is an important intermediate step in the selective catalytic reduction (SCR) of NOx to N2. These studies have prompted the development of schemes that use an oxidation catalyst to convert NO to NO2, followed by a reduction catalyst to convert NO2 to N2. Multi-stage SCR offers high NOx reduction efficiency from catalysts that, separately, are not very active for reduction of NO, and alleviates the problem of selectivity between NO reduction and hydrocarbon oxidation. A plasma can also be used to oxidize NO to NO2. This paper compares the multi-stage catalytic scheme with the plasma-assisted catalytic scheme for reduction of NOx in lean-burn engine exhausts. The advantages of plasma oxidation over catalytic oxidation are presented.

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MULTI-STAGE SELECTIVE CATALYTIC REDUCTION OF NO_x IN LEAN-BURN ENGINE EXHAUST

B. M. Penetrante, M. C. Hsiao, B. T. Merritt and G. E. Vogtlin
Lawrence Livermore National Laboratory

Abstract: Recent studies suggest that the conversion of NO to NO_2 is an important intermediate step in the selective catalytic reduction (SCR) of NO_x to N_2. These studies have prompted the development of schemes that use an oxidation catalyst to convert NO to NO_2, followed by a reduction catalyst to convert NO_2 to N_2. Multi-stage SCR offers high NO_x reduction efficiency from catalysts that, separately, are not very active for reduction of NO, and alleviates the problem of selectivity between NO reduction and hydrocarbon oxidation. A plasma can also be used to oxidize NO to NO_2. This paper compares the multi-stage catalytic scheme with the plasma-assisted catalytic scheme for reduction of NO_x in lean-burn engine exhausts. The advantages of plasma oxidation over catalytic oxidation are presented.

I. Introduction

Many studies suggest that the conversion of NO to NO_2 is an important intermediate step in the selective catalytic reduction (SCR) of NO_x to N_2 [1-5]. Some effort has been devoted to separating the oxidative and reductive functions of the catalyst in a multi-stage system [6]. This method works fine for systems that require hydrocarbon addition. The hydrocarbon has to be injected between the NO oxidation catalyst and the NO_2 reduction catalyst, as shown in Figure 1; otherwise, the first-stage oxidation catalyst will also oxidize the hydrocarbon and decrease its effectiveness as a reductant. The multi-stage catalytic scheme is appropriate for diesel engine exhausts since they contain insufficient hydrocarbons for SCR, and the hydrocarbons can be added at the desired location. For lean-burn gasoline engine exhausts, the hydrocarbons already present in the exhausts will make it necessary to find an oxidation catalyst that can oxidize NO to NO_2 but not oxidize the hydrocarbon.

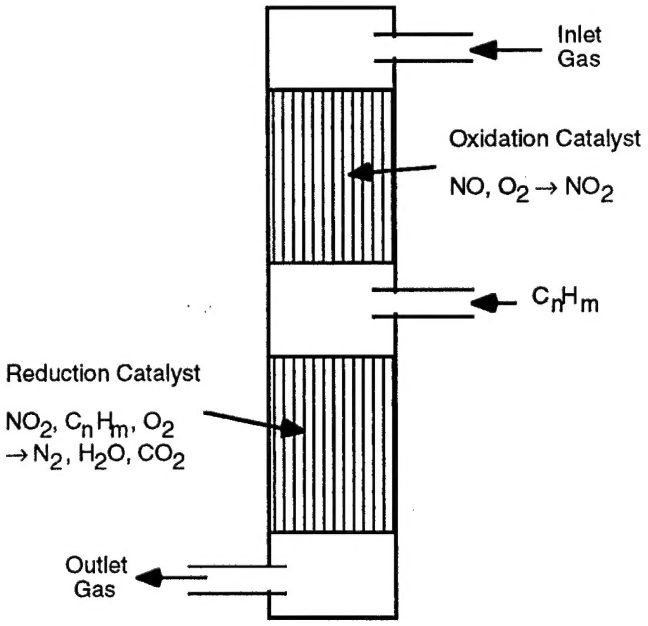

Figure 1. Multi-stage SCR scheme using an oxidation catalyst to convert NO to NO_2 and then a reduction catalyst to convert NO_2 to N_2.

A plasma can also be used to oxidize NO to NO_2. Plasma oxidation has several advantages over catalytic oxidation. Plasma-assisted catalysis can work well for both diesel engine and lean-burn gasoline engine exhausts. This is because the plasma can oxidize NO in the presence of hydrocarbons without degrading the effectiveness of the hydrocarbon as a reductant for SCR. In the

plasma, the hydrocarbon enhances the oxidation of NO, minimizes the electrical energy requirement, and prevents the oxidation of SO_2.

This paper discusses the use of multi-stage systems for selective catalytic reduction of NO_x. The multi-stage catalytic scheme is compared to the plasma-assisted catalytic scheme.

II. Multi-Stage Catalytic Scheme

The multi-stage selective catalytic reduction of NO_x is accomplished in two steps. First, an oxidation catalyst converts NO to NO_2 in the absence of a hydrocarbon:

oxidation catalyst + NO + $O_2 \rightarrow NO_2$

Then, a reduction catalyst reduces NO_2 to N_2 by selective reduction using hydrocarbons:

reduction catalyst+NO_2+HC $\rightarrow$ N_2+CO_2+H_2O.

Multi-stage SCR has several advantages over conventional SCR. First, the multi-stage scheme offers high NO_x reduction efficiency from catalysts that, separately, are not very active for reduction of NO. Second, the multi-stage scheme alleviates the problem of selectivity between NO reduction and hydrocarbon oxidation. The important NO_2 intermediate is formed without consuming the hydrocarbon reductant.

Figure 2 shows the FTIR spectra of the process for a model exhaust gas consisting of 500 ppm NO, 10% O_2 and balance N_2. The first-stage oxidation catalyst is Pt-based. The second-stage catalyst is essentially the same material but without the Pt. The hydrocarbon, 500 ppm (C_3) propene, is injected between the oxidation catalyst and the reduction catalyst. The temperature of both catalysts is 300°C.

The spectrum of the inlet gas is shown in the top box ("inlet") of Figure 2. Without the oxidation catalyst (i.e., first stage is removed), the NO_x reduction efficiency is very low, as shown in the second box ("outlet without oxidation catalyst"). The NO_x reduction at this temperature is very low even in the presence of a hydrocarbon reductant.

When the gas stream is first passed through the oxidation catalyst, the NO is oxidized to NO_2, as shown in the third box ("after first catalyst"). The NO_x reduction is still very low. The same amount of total NO_x (NO + NO_2) is left in the gas stream.

When the NO_2-containing gas stream from the first catalyst is mixed with the hydrocarbon reductant and then passed through the second catalyst, both the NO_x and the hydrocarbons are eliminated, as shown in the bottom box ("after second catalyst"). The NO_2 is chemically reduced to N_2 on the second catalyst.

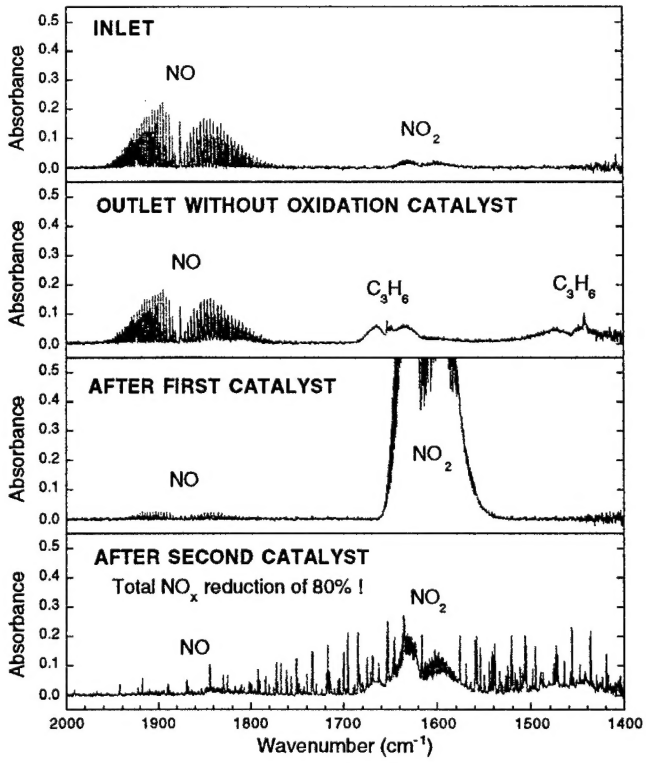

Figure 2. FTIR spectra showing the multi-stage selective catalytic reduction of NO_x.

III. Plasma-Assisted Catalytic Scheme

The oxidation of NO to NO_2 can also be accomplished with a plasma. The chemistry behind the plasma oxidation of NO is presented in an accompanying paper in this proceedings [7].

This section will present the advantages of plasma oxidation over catalytic oxidation.

The multi-stage catalytic scheme requires the injection of hydrocarbon between the NO oxidation catalyst and the NO_2 reduction catalyst. This is necessary because the oxidation catalyst will also oxidize the hydrocarbon and decrease its effectiveness as a reductant. The plasma can oxidize NO in the presence of hydrocarbons without degrading the effectiveness of the hydrocarbon as a reductant for SCR. Plasma-assisted catalysis therefore works well for both diesel engine and lean-burn gasoline engine exhausts. The hydrocarbon in the plasma is actually beneficial. In the plasma, the hydrocarbon enhances the oxidation of NO, minimizes the electrical energy requirement of the plasma reactor, and prevents the oxidation of SO_2. During the oxidation of NO to NO_2, the plasma oxidizes a fraction of the hydrocarbons, but leaves partially oxygenated hydrocarbon products that are as least as effective as the original hydrocarbons.

Catalytic oxidation has a limited temperature operating range. Figure 3 shows the efficiency for oxidation of NO to NO_2 by a Pt-based catalyst in a model exhaust gas consisting of 500 ppm NO, 10% O_2 and balance N_2. The oxidation efficiency maximizes at 250°C. The efficiency drops substantially at temperatures below 200°C. The efficiency also drops substantially at temperatures above 400°C. It is therefore important to match the temperature operating condition of the oxidation catalyst with that of the reduction catalyst.

Plasma oxidation of NO in the presence of hydrocarbons can have high efficiency over a wide range of temperatures. Figure 4 shows the efficiency for plasma oxidation of NO to NO_2 in a model exhaust gas consisting of 500 ppm NO, 1000 ppm (C_3) propene, 10% O_2 and balance N_2.

IV. Conclusions

Multi-stage SCR offers high NO_x reduction efficiency from catalysts that, separately, are not very active for reduction of NO, and alleviates the problem of selectivity between NO reduction and hydrocarbon oxidation. In multi-stage SCR, either an oxidation catalyst or a plasma can be used to convert NO to NO_2, followed by a reduction catalyst to convert NO_2 to N_2. The use of a plasma for the oxidation of NO offers several advantages over catalytic oxidation. The plasma method works well for both diesel engine and lean-burn gasoline engine exhausts. The plasma can oxidize NO in the presence of hydrocarbons without degrading the effectiveness of the hydrocarbon as a reductant for SCR.

V. Acknowledgments

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VI. References

[1] M. Shelef, C.N. Montreuil and H.W. Jen, *Catalysis Letters* **26** (1994) 277.

[2] K.A. Bethke, C. Li, M.C. Kung, B. Yang, et al., *Catalysis Letters* **31** (1995) 287.

[3] C. Yokoyama and M. Misono, *Journal of Catalysis* **150** (1994) 9.

[4] D.B. Lukyanov, G. Sill, J.L. Ditri and W.K. Hall, *Journal of Catalysis* **153** (1995) 265.

[5] T. Beutel, B.J. Adelman, G.D. Lei and W.M.H. Sachtler, *Catalysis Letters* **32** (1995) 83.

[6] M. Iwamoto, A.M. Hernandez and T. Zengyo, *Chemical Communications* Jan 7 (1997) 37.

[7] B.M. Penetrante, et al., "Effect of Hydrocarbons on Plasma Treatment of NO_x", Proceedings of the 1997 Diesel Engine Emissions Reduction Workshop.

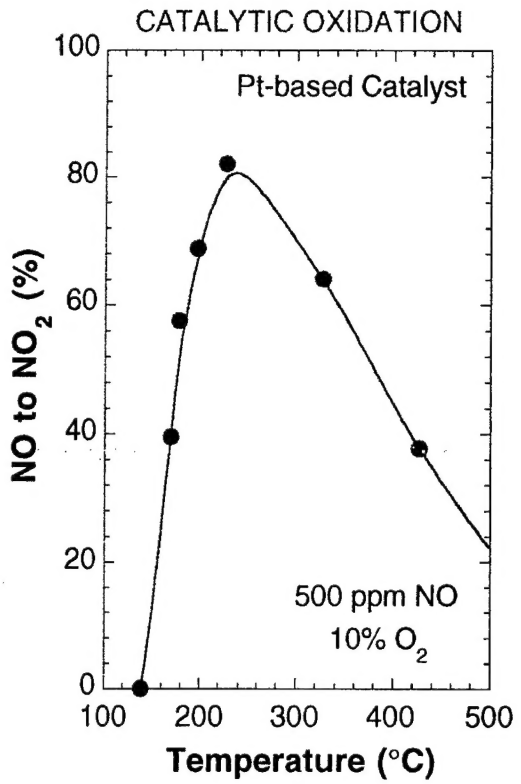

Figure 3. NO to NO_2 oxidation efficiency of a Pt-based catalyst for a model exhaust gas.

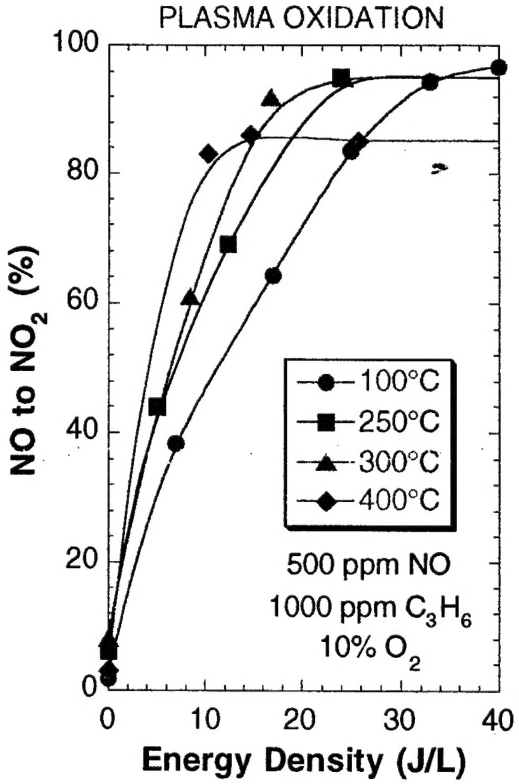

Figure 4. Effect of temperature and input electrical energy density on the efficiency for plasma oxidation of NO to NO_2 in a model exhaust gas.